

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Aromatic Amines as Co-sensitizers in Dye Sensitized Titania Solar Cells

Russell Gaudiana^a; Savvas Hadjikyriacou^a; Jin-An He^a; David Waller^a; Zhengguo Zhu^a

^a Konarka Technologies, Inc., Lowell, Massachusetts, USA

Online publication date: 10 July 2003

To cite this Article Gaudiana, Russell , Hadjikyriacou, Savvas , He, Jin-An , Waller, David and Zhu, Zhengguo(2003) 'Aromatic Amines as Co-sensitizers in Dye Sensitized Titania Solar Cells', *Journal of Macromolecular Science, Part A*, 40: 12, 1295 – 1306

To link to this Article: DOI: 10.1081/MA-120025309

URL: <http://dx.doi.org/10.1081/MA-120025309>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Aromatic Amines as Co-sensitizers in Dye Sensitized Titania Solar Cells

Russell Gaudiana,* Savvas Hadjikyriacou, Jin-An He,
David Waller, and Zhengguo Zhu

Konarka Technologies, Inc., Lowell, Massachusetts, USA

ABSTRACT

Solar cells based on titania require the use of sensitizing dyes in order to make the absorption band coincident with the solar spectrum. The most successful sensitizing dyes are based on Ru-bipyridyls and are chosen for their absorption and redox characteristics. In addition to absorbing visible light, the sensitizing dye injects an electron from its excited state into the band gap of the titania. The injected electron must be conducted through the titania to an electrode upon which the titania is coated. One of the energy wasting pathways available to the injected electron is back transfer to an oxidized dye species on the surface of the titania. We have discovered a simple means of alleviating this energy wasting pathway by anchoring aromatic amines, i.e., co-sensitizers, at low concentration along with the Ru-based bipyridyl sensitizing dye to the surface of titania nanoparticles. Our results indicate that there is a significant increase in cell efficiency ($\sim 15\%$ at AM 1.5, area $\geq 1 \text{ cm}^2$) primarily due to an increase in current when these species are present on the surface in combination with the dyes. We will report our preliminary results on a series of co-sensitizers, and we will compare these to literature findings which use similar compounds as either co-adsorbed species on titania or as substituents on the sensitizing dye molecule itself.

Key Words: Solar cells; Dye sensitized titania; Co-sensitizers; Aromatic amines.

*Correspondence: Russell Gaudiana, Konarka Technologies, Inc., Boott-Cotton Mills, 3rd Floor, 100 Foot-of-John St., Lowell, MA 01852, USA; Fax: 978-937-2062; E-mail: rgaudiana@konarkatech.com.



INTRODUCTION

Konarka Technologies is developing a roll-to-roll manufacturing process for dyed-sensitized, nanoparticle titania solar cells. For all practical product applications it is imperative that cell performance be as high as possible and should at least exceed a cell efficiency of 8–9% and preferably should be as high as 15%. Currently cell efficiency utilizing low temperature sintering procedures on polyethylene terephthalate (PET) substrate is ~5%, but we have attained 7–8% cell efficiency using high temperature sintering procedures on titanium foil. Over the past year, we have discovered several means of enhancing cell efficiency. One of these is done by anchoring aromatic amines along with sensitizing dyes to the titania surface. The simplest description of the function of these materials is that they act as co-sensitizers, i.e., electron donors, for the sensitizing dyes. The objective of Konarka's current research is to clarify the complex operative mechanism of electron transfer between the co-sensitizer, the sensitizing dye, and titania. This information will enable the optimization of the sensitizer structure so as to maximize its effect on cell performance.

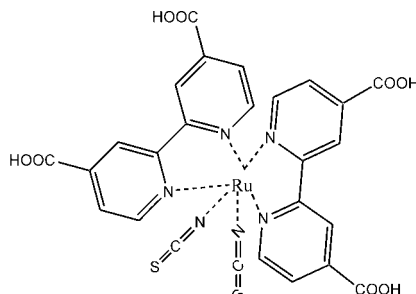
Our interest in solar energy has led us to attempt to make low cost solar cells by a roll-to-roll manufacturing process using dye-sensitized, titania nanoparticles which are interconnected by means of a low temperature sintering process. The dyes used for sensitizing the titania are typically Ru-bipyridyls and are chosen for their absorption and redox characteristics. The primary function of the dye is to sensitize titania to visible light by absorbing incident photons and injecting electrons from the excited state of the dye into the band gap of the titania. This phenomenon was first reported by O'Regan and Graetzel^[1] in the early 1990s. In order to produce current and perform useful work in an external load, the injected electron must be conducted through the titania to an electrode upon which the titania is coated. One of the energy wasting pathways available to the injected electron is back transfer to an oxidized dye species on the surface of the titania.

We have discovered a simple means of alleviating this energy wasting pathway by anchoring aromatic amines, referred to as co-sensitizers or donors, at low concentration along with the Ru-based bipyridyl sensitizing dye to the surface of titania nanoparticles. Our results indicate a significant increase in cell efficiency (~Δ12% at AM 1.5, area $\geq 1 \text{ cm}^2$) due primarily to an increase in current when these species are present on the surface in combination with the dyes. Since these results are in contradiction to other work on aromatic amines used as either co-adsorbed species on titania or as adducts to the sensitizing dye molecule itself, we propose to study the effects of structurally modified co-sensitizers on redox potential, incident photon to electron conversion efficiency (IPCE), and kinetics of electron transfer in an attempt to understand the photophysics of the co-sensitizer mechanism. In addition, these materials will continue to be tested in photovoltaic cells. The combined results will help guide the new design more effective co-sensitizers as well as new dyes which should lead ultimately to cells and modules with significantly higher performance.

All of the research that Konarka has conducted thus far uses the typical Ru-based, bipyridyl dye (see Structure I), developed by Graetzel et al.,^[2] at Ecole Polytechnique Federale de Lausanne (EPFL) over the last decade, as a sensitizing dye for titania solar cells.

Konarka also uses commercially available titania, which is made into an aqueous-based suspension, coated on either indium-tin oxide (ITO) glass plates or ITO coated PET. In all experiments, the titania coating was sintered at low temperature (<150°C) after





N3 : Ru(BipyridylCOOH)₂(N=C=S)₂

Structure I.

which it was sensitized with dye and/or a co-sensitizer by dipping in 8–50 mM solutions for about 30 min which establishes the equilibrium concentration. The equilibrium between adsorbed and dissolved dye/co-sensitizer depends on solvent, solution temperature, and the molecular structure of the co-sensitizer. After reaching equilibrium, the sensitized titania plate is removed from the dye sensitizing bath, the solvent is removed by evaporation, an electrolyte is added, the counter electrode is brought into contact with the electrolyte, laminated and sealed to complete the cell. A continuous coating process in which the dye sensitizing step takes place in <2 min has been developed for all of the steps just described with the exception of the incorporation of the co-sensitizer which will be part of the sensitizing dye solution.

As mentioned previously, Konarka has demonstrated that aromatic amines enhance the overall efficiency of photovoltaic cells when added to a sintered titania coating along with a sensitizing dye. The structures that Konarka has chosen are based on triphenyl amines containing one or more anchoring groups such as carboxylic acid or phosphoric acid groups. A representative sampling of the amine structures synthesized for this study thus far is shown in Table 1. All of these materials absorb in the near UV or short blue region of the spectrum. Although some of these compounds act as sensitizers by themselves, all of them require the presence a mid-visible sensitizing dye, such as N3, in order to exhibit any practical application as a solar cell.

There have been several attempts to enhance the performance of DSSCs by incorporating aromatic amines into cells. The basic idea is to provide a strong electron donor for the oxidized dye (sensitizer: S) which should prevent or at least slow the rate of back electron transfer from titania to the dye. In the generally accepted mechanism, the sensitizer absorbs a photon, reaches its first excited state [Eq. (1)], and injects an electron into TiO₂ [Eq. (2)]. This is followed by electron injection by the aromatic amine (donor: D) to the oxidized dye (S) [Eq. (3)] thereby reducing it back to its ground state. An energy-wasting step, which is significant in the absence of a donor, is back electron

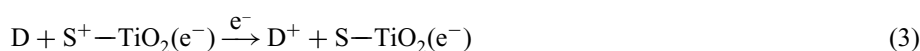
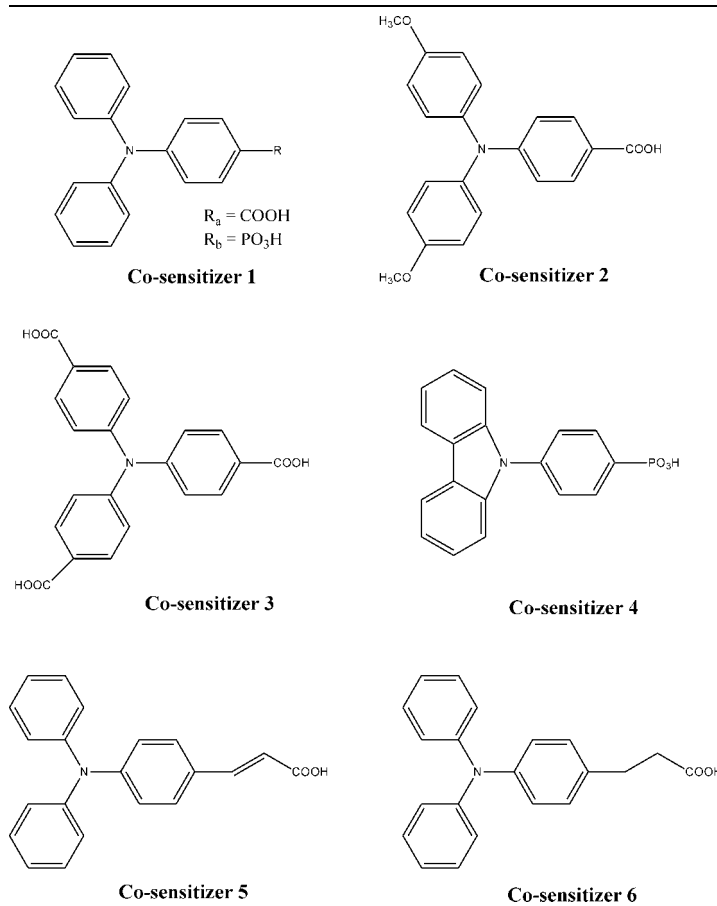


Table 1. Molecular structures of co-sensitizers synthesized for this study.

transfer from TiO_2 to the oxidized sensitizer [Eq. (4)]. However, in the presence of a donor,



Equation (4) should become significant. The resulting radical cation-based, aromatic amine is more stable than the oxidized form of the dye and back electron transfer to this species [Eq. (5)] should be slower than that to sensitizer.



In the literature there are three strategies for the donor/dye combination:

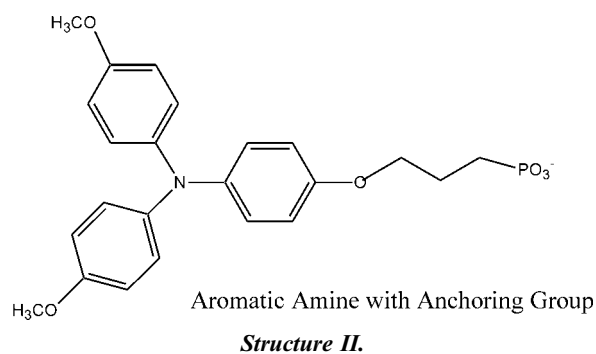
1. Aromatic amines (donors), separated by a non-conjugated chain from the terminal complexing group, e.g., phosphate, were bonded directly to the surface of the titania (see Structure II, "Aromatic Amine with Anchoring Group"). The strategy in this case is to remove the amine a short distance from the surface of the TiO_2 by means of an insulating chain, i.e., CH_2 groups. Since the rate of electron transfer decays exponentially with distance, back electron transfer from TiO_2 to the oxidized species was significantly reduced.
2. In the second strategy an aromatic amine is attached directly to the dye, which is bonded to the surface of the TiO_2 .^[3,4] In these examples, the donors are removed from the surface at a distance which is at least as large as in the previous example. Furthermore, the donor may be bonded directly to the dye, placing it in conjugation (see Structure III), or it may be bonded through a non-conjugated linkage, e.g., one or more CH_2 groups (see Structure IV).

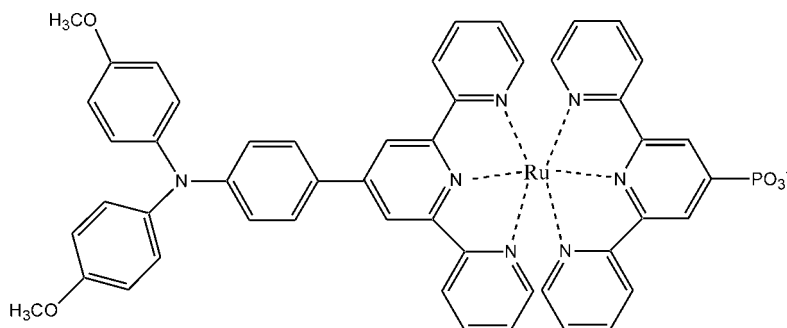
It should be noted that in Ref.^[4] the aromatic amine is a phenothiazine (see structure V, PTZ) which is bonded to the dye by a single CH_2 group, and carboxy groups, instead of a single phosphate group, are used to complex the dye to TiO_2 .

3. The third strategy simply involves the addition of donors, such as phenothiazines (see Structures V, "PTZ" and SV and VI, "MPTZ") to the electrolyte formulation.^[4]

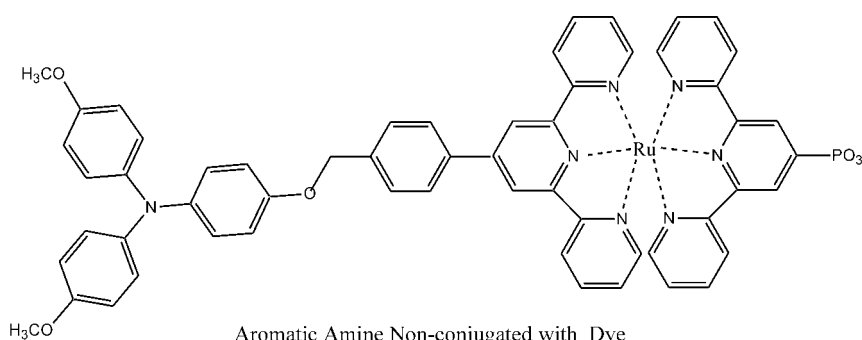
In regard to the first strategy, when the aromatic amine (II) was anchored to TiO_2 along with a Ru-based sensitizing dye, the quantum yield of electron injection (i.e., charge separation) is unity and the rates are high [Eqs. (2) and (3)]. Unfortunately, back electron transfer to the oxidized donor (D^+) is also very rapid. As a result, cell performance was not improved over cells containing the dye alone.

In regard to strategy 2, the first example is one in which the dye and the donor are in conjugation (III). In a cell, Structure III gives no better result than the parent dye itself. Detailed experiments indicate that this lack of enhancement is due to low injection efficiency, i.e., 60%, by the sensitizer [Eq. (2)]. In the example in which the donor is attached to the dye through a non-conjugated linkage, Structure IV, electron injection efficiency is 100% and very fast, but another energy wasting path was observed, namely, charge percolation through the monolayer of donor/dye.^[3] In fact, in the system in which





Aromatic Amine Conjugated to Dye

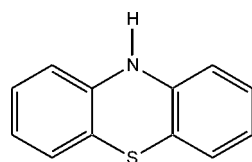
Structure III.

Aromatic Amine Non-conjugated with Dye

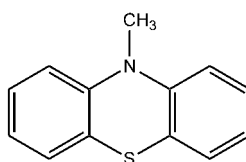
Structure IV.

the donor and the sensitizing dye are co-adsorbed (strategy 1), the latter being greater than or equal to 50% coverage of the available surface in order to exceed the percolation threshold, charge percolation in the monolayer of donors is also observed.^[5]

In another study in which a phenothiazine donor was attached through a non-conjugated link to a Ru-based sensitizing dye similar results to those cited above were obtained (see Structure VII).^[4] Specifically, electron transfer from the donor to the oxidized sensitizer proceeds rapidly and the resulting charge separated donor/sensitizer

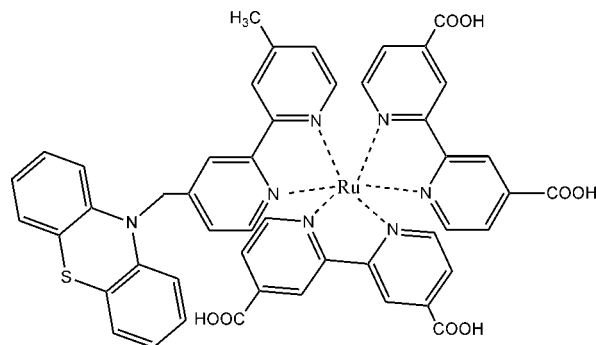


PTZ

Structure V.

MPTZ

Structure VI.



Structure VII.

pair is long lived (300 us). Although cell efficiency values are not given, the open circuit voltage measured for TiO₂ PV cells is ~100 mV higher than that for cells comprising sensitizing dyes alone.

In strategy 3, where the co-sensitizers (Structures V and VI) are added to the electrolyte, the association between the two is clearly evident from the kinetics of charge injection and transfer which are very high, and charge separated lifetimes are long [refer to Eqs. (2) and (3) in Ref.^[4]]. Unfortunately, back electron transfer to the oxidized phenothiazine donor is also very rapid. The authors postulate that this is due to the inability of the donor to escape from the sensitizer complex as evidenced by extremely low values IPCE, e.g., 1%. Incident photon to electron charge injection efficiency values for Structure VII are 45%. Attempts were made to affect donor/sensitizer separation by changing the solvent, ionic strength, and the donor structure but were not successful.

RESULTS AND DISCUSSION

In this initial phase of our research program, we tested triphenyl amine as an additive to an electrolyte formulation of a solar cell. Under the conditions of the test, the results indicate that there was no improvement over the control electrolyte. A similar result was observed by Bignozzi and Meyer,^[4] using phenothiazines as additives (strategy 3).

Our approach has been to concentrate on co-sensitizers containing primarily carboxylic anchoring groups. In most of the structures synthesized for this study (Table 1, co-sensitizers 1–4) these anchoring groups were placed directly on the phenyl ring of the amine moiety without insulating groups. In all cases, we used low temperature sintered titania on ITO-coated glass plates. A ruthenium dye, designated as N3 (Structure I), was used exclusively as the sensitizer along with co-sensitizers containing anchoring groups. Since co-sensitizers bonded directly to similar ruthenium dyes showed no,^[3] or only modest success,^[4] in regard to cell performance, and from a synthetic standpoint these structures are more difficult to synthesize, we decided not to pursue them.

We restricted our investigation to co-sensitizer concentration ranges which were significantly lower than the sensitizing dye. This strategy was used because it had been shown that when the co-sensitizer is present in molar ratios $\geq 50\%$, percolation of charge



among the co-sensitizers in the monolayer on the surface of the TiO₂ is a dominant mechanism. The percolation threshold is ~50 mol% and is aided by the nearly planar structure of the triphenyl amine and its oxidized radical cation. This geometry aids co-facial intermolecular association, i.e., stacking, which is necessary for charge migration.^[3,5] In addition, the methylene chain provides a flexible tether to the surface which allows the amine moieties to flex and rotate until an optimum stacking conformation is found. Structures in which the anchoring group is bonded directly to the phenyl ring by a single bond can rotate but flexing is eliminated. This situation forces each amine to be locked into the irregular, non-planar titania surface thus preventing extensive face-to-face contact between neighboring amines and the long range order necessary for percolation.

Cell performance data and λ_{\max} values for co-sensitizers CS-1a through CS-6 are listed in Table 2. The data clearly show that the best values were obtained for CS-1a and 1b—the simplest of the structures. The negative values simply mean that the sample performs worse than the control which has sensitizing dye only with no co-sensitizer.

Attempting to derive structure property relationships from this data is impossible at this stage of the program simply due to the fact that we do not know the amount of material adsorbed on the titania; these experiments are underway.

However, we have generated some information, which illustrates the problem. The data indicates that the ratio of sensitizing dye to co-sensitizer in the sensitizing solution is not the ratio of these materials on the titania at equilibrium as suggested in one of the references.^[3] The equilibrium concentration depends on the solubility of each material in the solvent used and on its molecular structure of each. The actual adsorbed concentrations were determined by desorption of both dye and co-sensitizer by treatment of the sensitized titania with sodium carbonate followed by HPLC analysis of the extracts. Figure 1 shows the absorption spectra of the co-sensitizer CS-1a extracted from titania. The solvents listed are those used to establish equilibrium during sensitization. The figure indicates that when a very good solvent for both co-sensitizers and dye is used as the sensitization solvent, such as dimethylformamide (DMF), the equilibrium concentration of CS-1a on titania is significantly lower than its equilibrium concentration when a poorer solvent such as

Table 2. Spectral absorption (λ_{\max}) and cell parameters normalized to N3 control for co-sensitizers.

Co-sensitizer ^a	λ_{\max} (nm) ^b	V_{oc} (volts)	I_{sc} (mA/cm ²)	($\Delta\eta\%$) ^c
CS-1a	284, 329	0.74	11.70	12.3 ± 0.1
CS-1b	302	0.70	14.51	10.8 ± 0.1
CS-2	328	0.62	8.60	-14.5 ± 0.2
CS-3	344	0.72	9.25	-10.4 ± 0.2
CS-4	289	0.70	13.13	-9.09 ± 0.27
CS-5	370	0.74	9.89	1.46 ± 0.12
CS-6	303	0.73	10.55	-3.02 ± 0.17

^aLow temperature sintered TiO₂ (120°C, 10 min); glass substrates; [N3] = 0.5 mM in ethanol + optimum [co-sensitizer]; electrolyte solvent: 3-methoxy propionitrile.

^bEthanol.

^c η is cell efficiency; $\Delta\eta\% = \eta_{\text{exp}} - \eta_{\text{control}}/\eta_{\text{control}} (100)$; average of 3 cells.



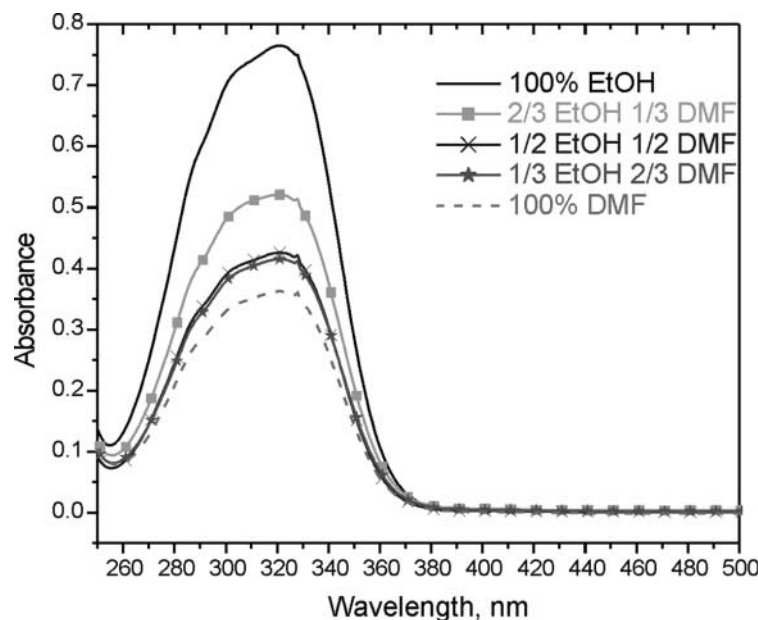


Figure 1. The equilibrium concentration of CS-1a on titania as a function of solvent used for sensitization.

ethanol is used. Subsequently, ethanol was used as the solvent in all co-sensitizer experiments.

In a closely related matter, we have observed a strong electrolyte effect on the ability of the co-sensitizers to enhance efficiency. The electrolyte formulations used contain strong, polar solvents, e.g., butyrolactone, sulfolane, 3-methoxypropionitrile, etc., and at this time we do not know if the variation in effectiveness of co-sensitizers, relative to CS-1a, is related to their energy states, their redox potentials or simply to a solvent effect. We plan to determine the equilibrium concentrations of all of the co-sensitizers in the presence of electrolytes in the near future.

In order to get some idea of the energetics of the interaction, we measured the redox potentials of N3 and four co-sensitizers in acetonitrile by means of cyclic voltammetry using the standard calomel electrode as a reference (Fig. 2). The data clearly show that the ground state energy level of CS-1a, 1b, and CS-3 are lower than N3, but that of CS-2 is slightly higher than that of the dye. This data suggests that if electron injection into the radical cation of N3 occurs from the ground state of a co-sensitizer, CS-2 would be the only material capable of this electron transfer. CS-3 would be the least likely to reduce N3 from its ground state due to the presence of three strong electron withdrawing groups. To add to the complexity of the situation, these redox potentials were measured in solution and at this time we do not have redox data of these materials on titania. These experiments will be completed soon.

Also shown in Fig. 2 are the calculated excited state energy levels of N3 and the co-sensitizers. The first excited singlet states of all the co-sensitizers listed are higher than that of N3, and therefore, each of them should be capable of injecting an electron into



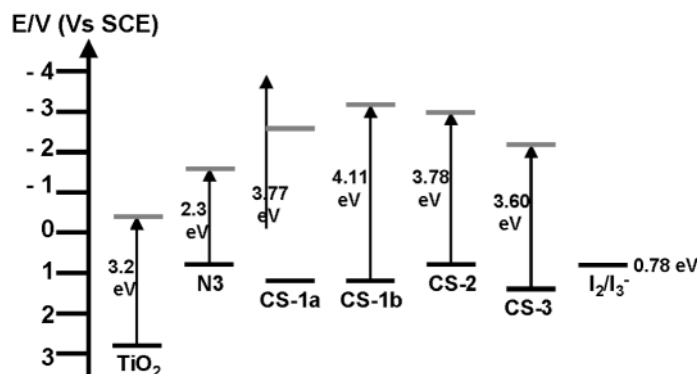


Figure 2. Energy level diagram of sensitizing dye (N3) and various co-sensitizers.

oxidized N3 dye. For this mechanism to be operative, however, the co-sensitizers would have to absorb energy. It will be noted from Fig. 3 that CS-1a does not absorb any light above 400 nm, and all of the other co-sensitizers (see Table 2 for λ_{max}) show similar absorption curves. Although the solar spectrum is weak at these short wavelengths, energy is available down to about 310 nm. In order to determine whether or not the excited state of the co-sensitizer CS-1a is necessarily involved in the electron transfer mechanism, we placed a filter, which cuts out all wavelengths below 450 nm, over the cell thereby preventing excitation of the co-sensitizer. Surprisingly, the effect is still operative, that is, cell performance increased ($\Delta\eta\% + 10.1\%$) in spite of the fact that the co-sensitizer was present only in its ground state. This suggests that the excited state of the co-sensitizers is not a requirement for electron transfer, but the latter may occur from the ground state of the co-sensitizer to the radical-cation of the dye.

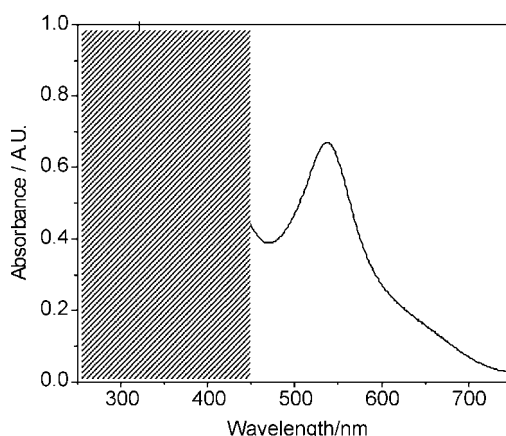


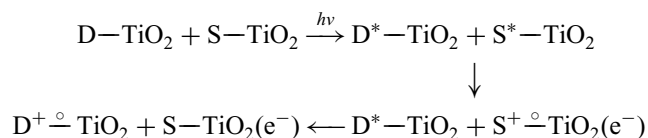
Figure 3. The composite absorption spectra of CS-1a (UV absorber) and N3 dye showing the absorption of the cut-off filter (diagonal lines).



There are three mechanisms that might be operative, all of which generate the same products, namely, the radical cation of the co-sensitizer (donor), the ground state of the sensitizing dye and a free electron in the titania nanocrystal.

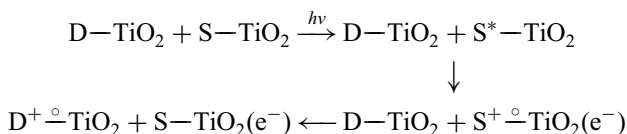
The first mechanism would involve excitation of both sensitizer (S) and co-sensitizer (D). However, as described previously, excitation of the donor is not a requirement for electron transfer since the cell performance increases relative to N3 control even when the co-sensitizer is not excited.

Mechanism 1



In the second mechanism, only the sensitizer is excited; it injects an electron into the titania, and subsequently the co-sensitizer donates an electron from its ground state to the sensitizer. In light of the ground state energies determined by cyclic voltammetry in solution, this mechanism is not energetically favored. There is one caveat, however, the

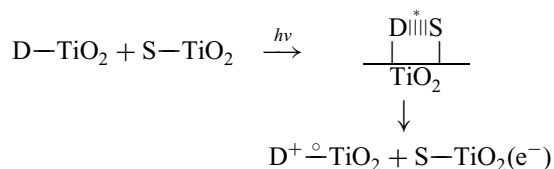
Mechanism 2



actual values of the ground and excited state energies when these species are anchored to titania are not known, and they may differ significantly.

Another mechanism that might operate is one in which the sensitizer and co-sensitizer form an excited state complex upon absorption of a photon (Mechanism 3) by the sensitizer. Injection of an electron from the excited state complex to the titania proceeds with concomitant generation of a ground state sensitizer and the radical cation of the co-sensitizer.

Mechanism 3



There are several examples in the literature describing exciplex formation between aromatic amines and non-planar transition metal complexes. Exciplex formation may occur between the ground state donor and either the ligand (ligand centered exciplexes) or the transition metal (metal centered exciplexes) of the complex.^[6-8] Electron transfer in these systems has also been documented.^[9-11]



CONCLUSION

Initial experimental results indicate that aromatic amines anchored to the surface of dye sensitized titania nanoparticles enhance the performance of photovoltaic solar cells. Although the specific operative mechanism by which this beneficial interaction occurs is not known in detail, it is clear from the limited data in-hand that electron transfer from the amine to the sensitizing dye is a key step. The co-sensitizers that show no effect or detract from cell performance may have adsorption/desorption equilibrium shifted in favor of the latter. Research is continuing to delineate this mechanism which should lead to further enhancement and optimization.

REFERENCES

1. O'Regan, B.; Graetzel, M. A low cost high efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, *353*, 737.
2. Recent review articles written by M. Graetzel are: Graetzel, M. Molecular photovoltaics that mimic photosynthesis. *Pure Appl. Chem.* **2001**, *73*, 459; Graetzel, M. Photoelectrochemical cells. *Nature* **2001**, *414*, 338.
3. Bonhote, P.; Moser, J.-E.; Humphrey-Baker, R.; Vlachopoulos, N.; Zakeeruddin, S.M.; Walder, L.; Graetzel, M. Long-lived photoinduced charge separation and redox-type photochromism on mesoporous oxide films sensitized by molecular dyads. *J. Amer. Chem. Soc.* **1999**, *121*, 1324.
4. Argazzi, R.; Bignozzi, C.A.; Heimer, T.A.; Castelano, F.N.; Meyer, G.J. Light-induced charge separation across Ru(II)-modified nanocrystalline TiO₂ interfaces with phenothiazine donors. *J. Phys. Chem. B* **1997**, *101*, 2591.
5. Bonhote, P.; Gogniat, E.; Tingry, S.; Barbe, C.; Vlachopoulos, N.; Lenzenmann, F.; Comte, P.; Graetzel, M. Efficient lateral electron transport inside a monolayer of aromatic amines anchored on nanocrystalline metal oxide films. *J. Phys. Chem. B* **1998**, *102*, 1498.
6. Ballardini, R.; Varani, G.; Balzani, V. Exciplexes of transition metal complexes. *J. Am. Chem. Soc.* **1974**, *96*, 7123.
7. Vogler, A.; Kunkely, H. Charge transfer exciplex emission involving a transition metal complex. *Inorg. Chim. Acta* **1980**, *45*, L265.
8. Horvath, A.; Stevenson, K.L. Transition metal complex exciplexes. *Coord. Chem. Rev.* **1996**, *153*, 57.
9. Bandyopadhyay, P.; Bharadwaj, P.K.; Basu Roy, M.; Dutta, R.; Ghosh, S. Photo-physical properties of tris-acetylpyrene derivative of a cryptand in different environments. *Chem. Phys.* **2000**, *255*, 325.
10. Wang, P.; Zakeeruddin, S.M.; Exnar, I.; Graetzel, M. High efficiency dye-sensitized nanocrystalline solar cells based on ionic liquid polymer gel electrolyte. *Chem. Comm.* **2002**, *2002*, 4.
11. Chittibabu, K.G.; Hadjikyriacou, S.; Li, L. Ionic liquid based gel electrolyte compositions for dye sensitized solar cells. Materials Research Society, Fall Meeting, Boston, MA, 2002.

